

Overview of electrochemistry

| | Equilibrium electrochemistry (no current flows) | Dynamic electrochemistry (current does flow) |
|---------------|--|--|
| Homogeneous | Thermodynamics of electrolyte solutions (PC09): <ul style="list-style-type: none"> electrolytic dissociation thermodynamics and activities of ions | Conductance of electrolytes (PhysChem12): <ul style="list-style-type: none"> electrolytic conduction mobilities of ions Kohlrausch laws |
| Heterogeneous | Thermodynamics of electrodes and Galvanic cells (PhysChem10): <ul style="list-style-type: none"> electrochemical cells cell and electrode potential types of electrodes | Kinetics of electrode reactions (PhysChem17): <ul style="list-style-type: none"> exchange current overpotential Tafel equation Butler-Volmer equation electrolysis batteries |

HETEROGENEOUS DYNAMIC ELECTROCHEMISTRY

- Observations** (current density–overpotential, exchange current(s), Tafel equation, ...)
- Interpretation of the observations** (the double layer and its models, Galvani and Volta potentials; kinetics of electrode reactions, Butler–Volmer equation; lower and upper limits of overpotential, polarization, limiting current)
- Practical electrochemistry** (working galvanic cells, accumulators, fuel cells, polarography, voltammetry, electrolysis, corrosion)

Kinetics of electrode processes (heterogeneous dynamic electrochemistry)

- In **equilibrium electrochemistry** (thermodynamics of electrolytes, Galvanic cells and electrodes), states of equilibrium and the possibilities of changes are described. No current flows in such systems, the Galvanic cell does no useful work, no change occurs on the electrodes.
 - In **non-equilibrium electrochemistry [dynamic electrochemistry]**, dynamic processes are described: the system is not in equilibrium: current flows in the solutions, substances deposit or dissolve on electrodes. In addition to equilibrium electrode potential, overpotential occurs.

Kinetics of electrode processes (heterogeneous dynamic electrochemistry)

- In **dynamic electrochemistry**, the voltage and current of spontaneous reactions in **Galvanic cells** or those of forced reactions in electrolysis are described in a temporal and spatial manner.
 - Understanding of the mechanism of electrode processes is necessary for both electrolysis and Galvanic cells.
 - Macroscopic measurements give important information about the processes on electrode surfaces and also contribute to understanding phenomena occurring at the molecular level.
- [Ionic conduction in an electrolyte solution is basically a transport process in an electric field. We discussed this earlier (lectures 11-12).]

1. Observations

- Equilibrium (current-free) potentials [lecture 10]:

 - The thermodynamic relationship between cell potential and standard reaction Gibbs free energy of the redox reaction is well-known:

$$-vFE_{cell}^{\ominus} = \Delta_r G^{\ominus}$$
 - The concentration dependence of equilibrium cell potential (e.m.f.) and electrode potential is known:

$$E_{cell} = E^{\ominus} - (RT/vF) \ln Q$$

$$E = E^{\ominus} + (RT/vF) \ln a_i \quad (\text{for electrode of the first kind})$$
 - Connection between e.m.f. and electrode potentials:

$$E_{cell} = E_{right} - E_{left} \quad \text{or} \quad E_{cell} = E_{cathode} - E_{anode}$$

1. Observations

- Quantities in dynamic electrochemistry:

a) **Current-related:**

 - The definition of reaction rate in a heterogeneous process: product flux = $k[\text{particle}]$
 - In the two electrode processes:

$$v_{ox} = k_c[\text{Ox}], \quad \text{and} \quad v_{red} = k_a[\text{Red}]$$
 - Characterization of the on an electrode: j
 - current density (j) = current / surface [A cm^{-2}]
 - [Remark: there is Ohmic resistance in systems like this (which is readily measurable).]

1. Observations

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Quantities in dynamic electrochemistry:

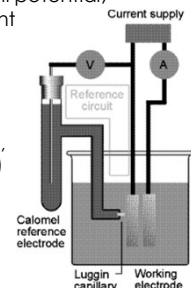
- b) **Potential / voltage related:** The original equilibrium electrode potentials (E) are not valid in a working Galvanic or electrolytic cell. The differences are formally described as:
 - **On electrodes:** η overpotential (polarization potential)
 - **In Galvanic cells:** actual cell potential or working potential ($< E$) [not necessarily constant, depends on the current]
 - **In electrolytic cells:** η overpotential ($> E$) [set by the experimenter based on the objectives]
 - All of these quantities are measurable – similarly to E .

1. Observations

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- In dynamic electrochemistry, the relationship between potential (electrode potential, cell potential, overpotential) and current (current density) is measured.

- For the measurements, reference electrodes are needed with constant potential. Today's automated instruments (potentiostats, amperostats, etc.) are able to keep the potential (V) or the current (A) constant or to change it in a controlled way.
- Many experimental arrangements are known, a basic type is shown in the figure:



1. Observations

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- Practical (industrial, analytical, household, etc.) electrochemistry is always non-equilibrium electrochemistry.
- The essence and usefulness of galvanic cells is that they act as a power source. In this case, it is always possible to calculate the working potential characteristic of the operating state.
- Electrolysis occurs only when an external voltage source is used, which has a higher potential value than the equilibrium cell potential (this higher potential is called overpotential).
- The example of rechargeable galvanic batteries is very clear: they provide a voltage less than the equilibrium cell potential of the Galvanic cell and can only be recharged with excess voltage over their e.m.f.

1. Observations

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Quantities in dynamic electrochemistry:

- c) **Current density, exchange current(s):**
 - Observations show that current density j changes when the overpotential η is changed: increase and decrease, even a sign change are possible.
 - On all electrodes, cathodic $j_c = Fk_c[\text{Ox}]$ and anodic $j_a = Fk_a[\text{Red}]$ current densities are. The actual (and measurable) current density j is the difference of these two:
 - if $j_a > j_c$, then $j > 0$, the net current is anodic,
 - if $j_a < j_c$, then $j < 0$, the net current is cathodic,
 - if $j_a = j_c$, then $j = 0$, the net current is zero. It can be given as: $|j_a| = |j_c| = |j_0|$

1. Observations

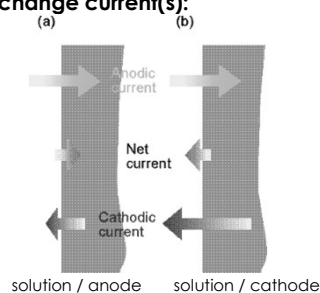
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Quantities in dynamic electrochemistry:

- c) **Current density, exchange current(s):**
 - (a) anodic and
 - (b) cathodic net current density:

$$j_a = Fk_a[\text{Red}]$$

$$j_c = Fk_c[\text{Ox}]$$



1. Observations

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- When $j_a = j_c$, then $j = 0$, i.e. in equilibrium, no current flow on the electrode.
- **But!** Similarly to other dynamic chemical equilibria (e.g. solution equilibria, solid/gas adsorption etc.), in equilibrium (no macroscopic current) both anodic and cathodic current flows through the system but their absolute values are the same and the directions are opposite.
- This is the j_0 exchange current density (or simply just exchange current).
- **Attention!** The j_0 exchange current is macroscopically zero, but molecularly an existing value!

1. Observations

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Quantities in dynamic electrochemistry:

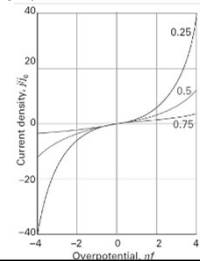
- a) **Relationship between the overpotential and current density: the Tafel equation:**
 - At small overpotential, current density increases linearly with the overpotential: $j = j_0 f \eta$ ($f = F/RT$)
 - At intermediate overpotential, the relationship is exponential (logarithmic). This is the **observed Tafel equation**: $j = j_0 e^{(1-\alpha)f\eta}$, $\ln j = \ln j_0 + (1-\alpha)f\eta$
 - At large overpotential, current density reaches an upper limit, this is the **limiting current**.
- If $\eta < 0$, then $j < 0$: $\ln(-j) = \ln j_0 - \alpha f \eta$

1. Observations

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Quantities in dynamic electrochemistry:

- a) **Cases in the overpotential–current density landscape, the Tafel equation:**
 - Current density j as a function of overpotential η :



1. Observations

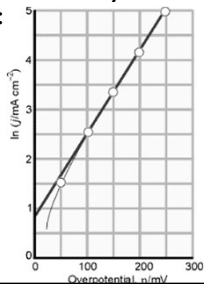
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Quantities in dynamic electrochemistry:

- a) **Cases in the overpotential–current density landscape, the Tafel equation:**

- Plot of the Tafel equation:

$$\ln j = \ln j_0 + (1-\alpha)f\eta$$



2. Interpretation of observations

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To interpret the observations, we need:

- an understanding of the structure of the surface boundary between the electrode and the electrolyte: a description of the electric double layer and the Nernst adsorption layer.
- the mechanisms of the rate limiting step: the activation free energy $\Delta^\ddagger G$ of the charge transfer step and its possible dependence on the overpotential η .
- to clarify the role of diffusion and activation. Recognizing the relationship between η and $\Delta^\ddagger G$ is the core issue in the kinetic description of electrode processes.

2. Interpretation of observations

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- a) **The structure of the electrode/electrolyte boundary:**

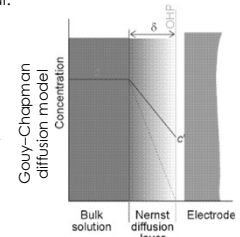
- In the bulk solution, the flow of the solute toward (and from) the surface is caused by (fast) convection (stirring).
- On a solid-liquid boundary, there is always a highly adhesive liquid layer (not only for electrolytes and not only on electrodes): this is the **Nernst δ diffusion layer**. In this layer, transport of matter is only possible by (slow) diffusion, so a concentration gradient forms in it.
- There is no specific structure in it. Its width depends on the intensity of stirring or rotation – 10^{-3} - 10^{-2} mm. [On a rotating disc electrode: $\delta = D^{1/3} \eta^{1/6} \omega^{-1/2}$].

2. Interpretation of observations

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- a) **The structure of the electrode/electrolyte boundary:**

- In the case of electrodes – with charges (ions) in both the solid electrode and in the solution – charge separation occurs resulting in the formation of an electric double layer. It can be measured by measuring the electrode potential.
- This electric double layer is formed within a narrow layer close to the phase boundary in the δ Nernst diffusion layer. One part of this layer is the surface of the metal electrode, where there is a (positive or negative) "charge surplus,..". The other is the electrolyte layer where – unlike the bulk phase of the solution – the spatial distribution of the charged ions is not uniform.



2. Interpretation of observations

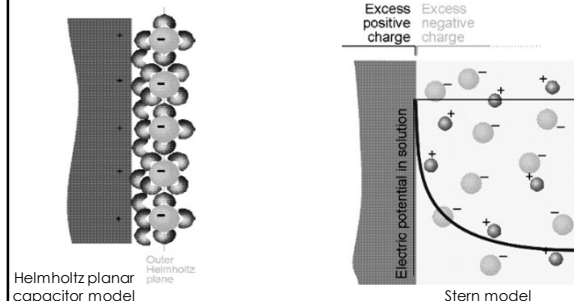
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- a) **The structure of the electrode/electrolyte boundary:**
- The thickness of the electric double layer is some ten times of the diameter of the hydrated ion or solvent molecule and this layer exhibits a specific structure.
 - The structure of the double layer can be described by three models:
 - the Helmholtz planar capacitor model,
 - the Gouy–Chapman diffusion model and
 - the combination of the two i.e. the Stern model.
 - The Nernst diffusion layer and the Helmholtz electric double layer on the electrode surface. →

2. Interpretation of observations

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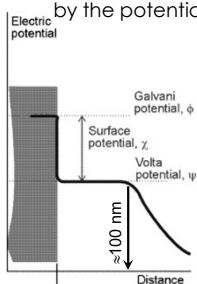
- a) **The structure of the electrode/electrolyte boundary:**



2. Interpretation of observations

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- a) **The structure of the electrode/electrolyte boundary:**
- Within the double layer, electric field is characterized by the potential of a unit charge (e^-) vs. the surface.
 - On approaching from a large distance, the potential increases exponentially, then remains constant close to the (quasi-planar) surface (ψ Volta potential).
 - A sudden jump on the surface (χ surface potential).
 - Together: ϕ Galvani potential.
 - Only the Galvani potential is available experimentally, it is the same as the electrode potential.



2. Interpretation of observations

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- a) **The structure of the electrode/electrolyte boundary:**
- The μ chemical potential of ions in the ϕ electric field changes: we are now talking about μ^* electrochemical potential; $\mu^* = \mu + zF\phi$
 - This is exactly the potential increase seen with the Volta potential: the electrochemical potential increases as the ion approaches from the bulk to the charged electrode surface.
 - [When $\phi = 0$, then the electrochemical potential is obviously equal to the chemical potential.]

2. Interpretation of observations

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- a) **The structure of the electrode/electrolyte boundary:**
- These two (diffusion and electric) layers have an important role in the electrode processes.
 - In the case of high overpotential, the rate of electrode process is determined by ion diffusion through the Nernst diffusion layer – independent of the electrode potential: this is the so-called **diffusion kinetics** because the ions with high potential can precipitate (can be reduced) fast.
 - In medium overpotential values, the rate of the electrode process is determined by the rate of charge (ions) crossing on the electrode surface: this is a so-called **activation kinetics**.
 - [like **diffusion-** and **energy limited** reactions in solutions (lecture PC15, slide 13)!]

2. Interpretation of observations

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- b) **Kinetics of electrode processes, the Butler–Volmer equation:**

For both currents, the **current density** can be given:

- cathodic current density: $j_c = Fk_c[\text{Ox}]$
- anodic current density: $j_a = Fk_a[\text{Ox}]$
- [In dynamic equilibrium: $j_0 = j_a = -j_c$]
- The **rate constant** k needs to be interpreted (as was the case with homogeneous reactions).

The key recognition: the **activated complex theory** is also valid for electrode processes:

$$k = Be^{-\frac{\Delta G^\ddagger}{RT}}, \text{ so } j = FB[\text{Ox}]e^{-\frac{\Delta G^\ddagger}{RT}}$$

2. Interpretation of observations

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b) Kinetics of electrode processes, the Butler-Volmer equation:

- The η overpotential (polarization) influences the activation of the electrode process, so η modifies the Gibbs free energy of activation in the exponent of rate constant k :

$$\Delta^\ddagger G = \Delta^\ddagger G(0) \pm \alpha z F \eta$$

- In this formula, α is the so-called **transmission factor**, its value lies in the range 0 to 1, experimentally often found to be about 0.5.

$$k = B e^{-\Delta^\ddagger G / RT} \quad j = F B [\text{Ox}] e^{-\Delta^\ddagger G / RT}$$

- Based on this we look for the relation of j and η .

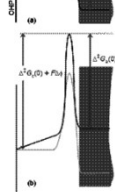
2. Interpretation of observations

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b) Kinetics of electrode processes, the Butler-Volmer equation:

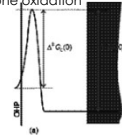
- the transition state resembles a species that has undergone reduction

$$\alpha = 1$$



the transition state resembles a species that has undergone oxidation

$$\alpha = 0$$



activation profiles of reduction-oxidation

- normal reaction profile
- potential difference between the inner and outer Helmholtz layer
- the electron transport appears either in the activation or in the reaction free energy

2. Interpretation of observations

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b) Kinetics of electrode processes, the Butler-Volmer equation:

- If in the electrode reaction $\text{Ox} + e^- = \text{Red}$ (cathodic reduction), the electrode becomes more positive (is polarized), the activation free energy of the electrode process increases:

$$\Delta^\ddagger G_c = \Delta^\ddagger G_c(0) + \alpha F \eta$$

- In a $\text{Red} - e^- = \text{Ox}$ oxidation (anodic) process, the effect of polarization: $\Delta^\ddagger G_a = \Delta^\ddagger G_a(0) - (1-\alpha) F \eta$
- With these two modified values of activation free energy, the net current density is obtained, which connects j and η . This is called the **Butler-Volmer equation**:

2. Interpretation of observations

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b) Kinetics of electrode processes, the Butler-Volmer equation:

- Without any overpotential ($\eta = 0$), the formula gives the exchange current density j_0 arising from the equilibrium cell potential E_{rev} without current: $j_0 = j_a = -j_c$

$$j_a = F B_a [\text{Red}] e^{-[\Delta^\ddagger G_a + (1-\alpha) F E] / RT}$$

$$j_c = F B_c [\text{Ox}] e^{-[\Delta^\ddagger G_c - \alpha F E] / RT}$$

- Exchange current density j_0 is not measurable directly, but can be extrapolated based on the Tafel equation ($\eta \rightarrow 0$). The introduction of j_0 gives a simpler form for the Butler-Volmer equation:

$$j = j_0 [e^{(1-\alpha) f \eta} - e^{-\alpha f \eta}]$$

2. Interpretation of observations

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b) Kinetics of electrode processes, the Butler-Volmer equation:

$$j = j_a - j_c = F B_a [\text{Red}] e^{-[\Delta^\ddagger G_a + (1-\alpha) F \eta] / RT} - F B_c [\text{Ox}] e^{-[\Delta^\ddagger G_c - \alpha F \eta] / RT}$$

$$j = j_0 [e^{(1-\alpha) f \eta} - e^{-\alpha f \eta}]$$

2. Interpretation of observations

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b) Kinetics of electrode processes, the Butler-Volmer equation:

- The effect of overpotential is well illustrated here:
 - 1 V potential increase
 - change the current density by 9 orders of magnitude,
 - which causes approx. 50 kJ mol⁻¹ Gibbs free energy of activation increase: this has a huge effect on the value of k !

2. Interpretation of observations

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e) Limits of the overpotential:

- The lower limit of overpotential:
 - At low overpotentials of $\eta \ll 0.01$ V, i.e. $f\eta \ll 1$, series expansion ($e^x = 1 + x + \dots$) gives:

$$j = j_0 [1 + (1-\alpha)f\eta + \dots - 1 - (-\alpha f\eta) - \dots] \approx j_0 f\eta$$
 - Ohm's law is valid in this regime, and – in agreement with the observations – a linear relationship is found between j and η .

$$j = j_0 [e^{(1-\alpha)f\eta} - e^{-\alpha f\eta}]$$

2. Interpretation of observations

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e) Limits of the overpotential:

- Upper limit of the overpotential:
 - At $\eta > 0.12$ V (intermediate anodic overpotential), the second term in the Butler–Volmer equation becomes negligible, so

$$j = j_0 e^{(1-\alpha)f\eta}, \text{ i.e.: } \ln j = \ln j_0 + (1-\alpha)f\eta.$$
 - At $\eta < -0.12$ V (intermediate cathodic overpotential), the first term becomes negligible, so

$$j = -j_0 e^{-\alpha f\eta}, \text{ i.e.: } \ln(-j) = \ln j_0 - \alpha f\eta.$$

These are the same as the **Tafel equation**. The transfer coefficient α and exchange current density j_0 can be determined in this way:

$$j = j_0 [e^{(1-\alpha)f\eta} - e^{-\alpha f\eta}]$$

2. Interpretation of observations

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d) Limiting current:

- At high overpotentials, the Nernst diffusion layer quickly becomes depleted because of the fast charge transfer (metal deposition). A further increase in η cannot increase the current density any more, as diffusion across the Nernst layer becomes the limiting step. This is characterized by the j_{lim} **limiting current density**.
- Its value only depends on the concentration gradient dc/dx , diffusion constant D , and layer thickness δ :

$$j_{lim} = zFJ_{lim} = \frac{zFDc}{\delta}$$

2. Interpretation of observations

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d) Limiting current:

- j_0 is a very important practical feature of the electrode:
 - if its value is high, the electrode hardly polarizes (this is an important criterion for good reference electrodes),
 - if j_0 is small, the electrode is easily polarized.
- On the high exchange current density Cu/Cu²⁺ electrodes – not too far from the equilibrium potential – the most inhibited step of the electrode process is the diffusion transport of Cu²⁺ (diffusion kinetics).
- Mixing affects the thickness of the diffusion layer, and thereby the value of the limiting current density.

3. Practical electrochemistry

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a) The practical significance of overpotential:

- Ion reactions do not really start at the reversible potentials. For cations, more negative, for anions, more positive potentials are needed. E.g.
 - H₂ production on Pt: 0 V, Pb: 0.6 V, Hg: 0.8 V.
 - O₂ production on Pt: 0.4 V, Pb: 0.3 V.
- The overpotential adds to the energy needs of electrolysis, so minimizing it is an important objective.
- Electrode process can be tuned by the proper selection of the electrode: we can decide which reaction to take place in solution electrolysis.

3. Practical electrochemistry

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b) Working Galvanic cells:

- In working Galvanic cells ($I > 0$), the **working potential of the cell** E' is always smaller than the equilibrium cell potential E_{cell} without current ($I = 0$) (electromotive force):

$$E' = \Delta\Phi_{right} - \Delta\Phi_{left} = E_{cell} + \eta_{right} - \eta_{left} - IR_s.$$

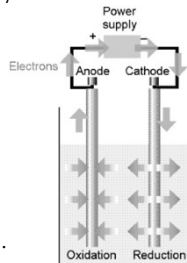
- The term IR_s (Ohmic term) gives the heat production within the solution as a result of the current. This causes energy loss in the Galvanic cell.

3. Practical electrochemistry

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e) **Electrolysis:** In an electrolytic cell, the potential necessary to force the reaction is larger than the equilibrium potential (**overpotential**).

- Faraday's laws of electrolysis:
 - i. The electric charge necessary to force 1 mol of electron is $F = 96485 \text{ C}$ (Faraday's constant).
 - ii. The mass of the substance produced by electrolysis is directly proportional to the current and the electrolysis time: $m = F \cdot I \cdot t$ (coulombmetry).



3. Practical electrochemistry

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- e) **Practical applications:**
- NaCl (common salt) electrolysis in industry (*Hg cathode, diaphragm*)
 - Electrolysis of molten $\text{Al}_2\text{O}_3 \rightarrow$ production of Al
 - Galvanization, (protective) metal layers
 - Electropolishing copper
 - Anodic oxidation of Al layers: metal protection
 - ...

3. Practical electrochemistry

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e) **Electrochemical corrosion:**

- O_2 is reduced, gains electrons from the metal

